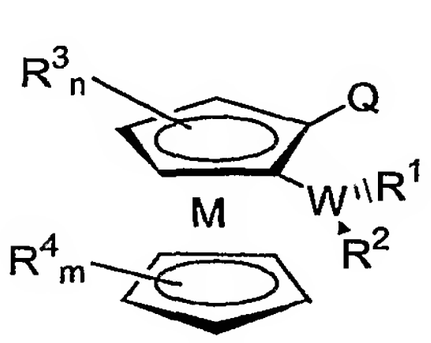
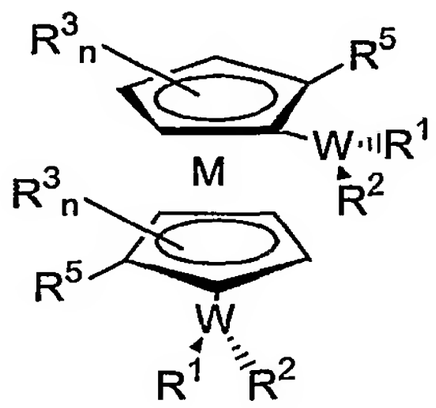
CLAIMS

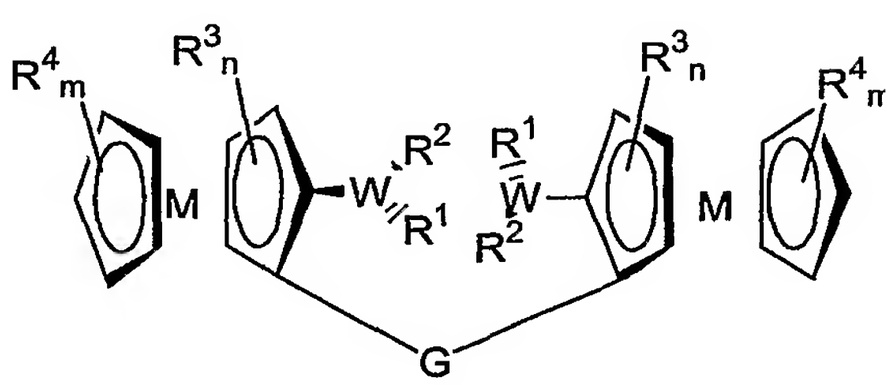
1. A metallocene-based phosphine or arsine ligand chiral at phosphorus or arsenic having the Formula (I), (II) or (III):



(I)



(II)



(III)

wherein

W is phosphorus or arsenic;

M is a metal;

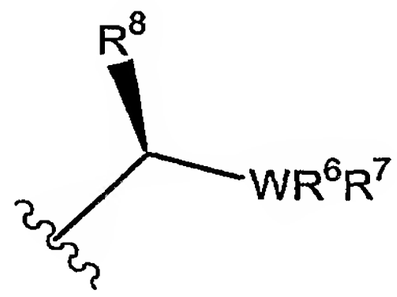
R^1 and R^2 are different from each other, and are independently selected from substituted and unsubstituted, branched- and straight-chain alkyl, alkoxy, alkylamino, substituted and unsubstituted cycloalkyl, substituted and unsubstituted cycloalkoxy, substituted and unsubstituted cycloalkylamino, substituted and unsubstituted carbocyclic aryl, substituted and unsubstituted carbocyclic aryloxy, substituted and unsubstituted heteroaryl, substituted and unsubstituted heteroaryloxy, substituted and unsubstituted carbocyclic arylamino and substituted and unsubstituted heteroarylamino, wherein the or each heteroatom is independently selected from sulphur, nitrogen, and oxygen;

R^3 and R^4 are the same or different, and are independently selected from substituted and unsubstituted, branched- and straight-chain alkyl, substituted and unsubstituted cycloalkyl, substituted and unsubstituted carbocyclic aryl, and substituted and unsubstituted heteroaryl wherein the or each heteroatom is independently selected from sulphur, nitrogen, and oxygen;

n is 0 to 3;

m is 0 to 5;

Q is selected from:

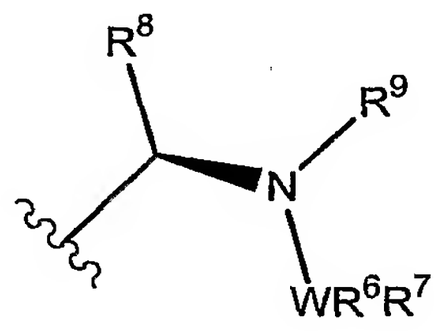


wherein W is phosphorus or arsenic;

R^6 and R^7 are the same or different, and are independently selected from substituted and unsubstituted, branched- and straight-chain alkyl, alkoxy, alkylamino, substituted and unsubstituted cycloalkyl, substituted and unsubstituted cycloalkoxy, substituted and unsubstituted cycloalkylamino, substituted and unsubstituted carbocyclic aryl, substituted and unsubstituted carbocyclic aryloxy, substituted and unsubstituted heteroaryl, substituted and unsubstituted heteroaryloxy, substituted and unsubstituted carbocyclic arylamino and substituted and unsubstituted heteroarylamino, wherein the or each heteroatom is independently

selected from sulphur, nitrogen, and oxygen; and R^8 is selected from hydrogen, substituted and unsubstituted, branched- and straight-chain alkyl, substituted and unsubstituted cycloalkyl, substituted and unsubstituted carbocyclic aryl, and substituted and unsubstituted heteroaryl wherein the or each heteroatom is independently selected from sulphur, nitrogen, and oxygen; or

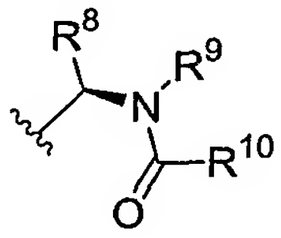
Q is selected from:



wherein W is phosphorus or arsenic;

R^6, R^7 and R^8 are, independently, as previously defined; and R^9 is selected from hydrogen, substituted and unsubstituted, branched- and straight-chain alkyl, substituted and unsubstituted cycloalkyl, substituted and unsubstituted carbocyclic aryl, and substituted and unsubstituted heteroaryl wherein the or each heteroatom is independently selected from sulphur, nitrogen, and oxygen; or

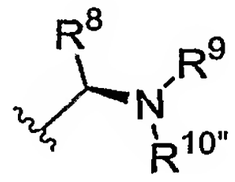
Q is selected from:



wherein R^6, R^7, R^8 and R^9 are, independently, as previously defined; and R^{10} is selected from hydrogen, substituted and unsubstituted,

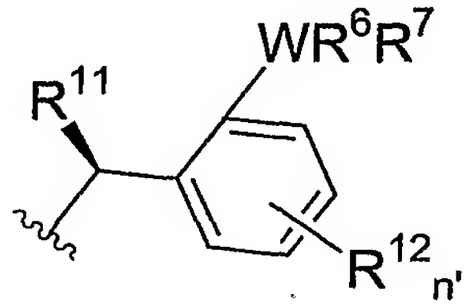
branched- and straight-chain alkyl, substituted and unsubstituted cycloalkyl, substituted and unsubstituted carbocyclic aryl, and substituted and unsubstituted heteroaryl wherein the or each heteroatom is independently selected from sulphur, nitrogen, and oxygen; or

Q is selected from:



wherein R^6, R^7, R^8 and R^9 are, independently, as previously defined; and $R^{10"}$ is selected from hydrogen, substituted and unsubstituted, branched- and straight-chain alkyl, substituted and unsubstituted cycloalkyl, substituted and unsubstituted carbocyclic aryl, and substituted and unsubstituted heteroaryl wherein the or each heteroatom is independently selected from sulphur, nitrogen, and oxygen; or

Q is selected from:

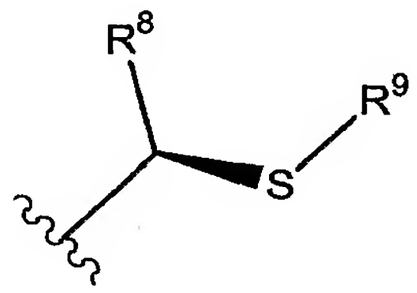


wherein W is phosphorus or arsenic;

R^6, R^7 are, as previously defined; R^{11} is selected from OR^{13}, SR^{13}, NHR^{13}, $NR^{13}R^{14}$, wherein R^{13} and R^{14} are the same or different and are independently selected from hydrogen, substituted and

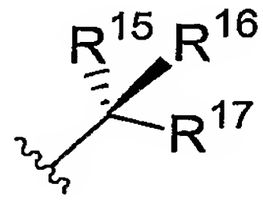
unsubstituted, branched- and straight-chain alkyl, substituted and unsubstituted cycloalkyl, substituted and unsubstituted carbocyclic aryl, and substituted and unsubstituted heteroaryl wherein the or each heteroatom is independently selected from sulphur, nitrogen, and oxygen; R^{12} is selected from hydrogen, halogen, OR^{13}, SR^{13}, $NR^{13}R^{14}$, substituted and unsubstituted, branched- and straight-chain alkyl, substituted and unsubstituted cycloalkyl, substituted and unsubstituted carbocyclic aryl, and substituted and unsubstituted heteroaryl wherein the or each heteroatom is independently selected from sulphur, nitrogen, and oxygen; wherein R^{13}, R^{14} are, as previously defined and n' is 0 to 4;

or Q is selected from:



wherein R^8 and R^9 are as previously defined;

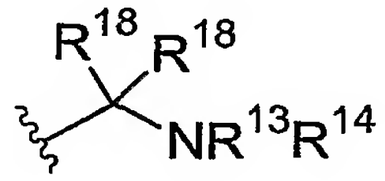
R^5 is selected from:



wherein R^{15}, R^{16} and R^{17} are the same or different and are independently selected from hydrogen, OR^{13}, SR^{13}, $NR^{13}R^{14}$, substituted and unsubstituted, branched- and straight-chain alkyl, substituted and unsubstituted cycloalkyl, substituted and

unsubstituted carbocyclic aryl, and substituted and unsubstituted heteroaryl wherein the or each heteroatom is independently selected from sulphur, nitrogen, and oxygen; wherein R^{13}, R^{14} are, as previously defined; or

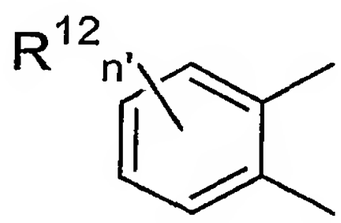
R^5 is selected from:

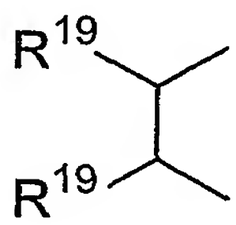


wherein R^{13}, R^{14} are as previously defined; the two geminal substituents R^{18} together are a doubly bonded oxygen atom (i.e. $(R^{18})_2$ is =O), or each substituent R^{18} on its own is hydrogen; and

G is selected from the group consisting of:

-CONH-R*-NHCO-, -CO-OR*O-CO-, -CO-R*CO-, -CH=N-R*-N=CH-, -CH_2NH-R*-NHCH_2-, -CH_2NHCO-R*-CONHCH_2-, -CH(R^8)NH-R*-NH(CH(R^8)-, -CH(R^8)NHCO-R*-CONHCH(R^8)-, -CONH-R-NHCO-, -CO-ORO-CO-, -CO-RCO-, -CH=N-R-N=CH-, -CH_2NH-R-NHCH_2-, -CH_2NHCO-R-CONHCH_2-, -CH(R^8)NH-R-NH(CH(R^8)-, -CH(R^8)NHCO-R-CONHCH(R^8)-; wherein R^8 is, independently, as previously defined; -R*- and –R- are selected from the group consisting of:

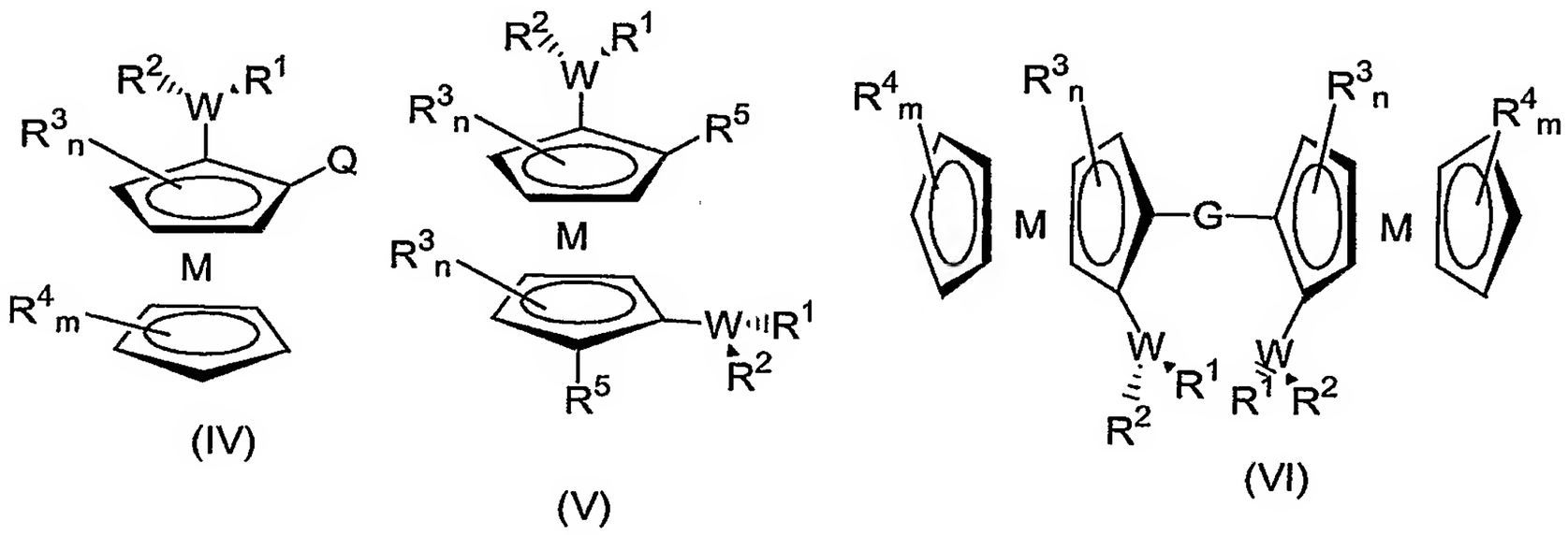




wherein R^{12} is as previously defined; R^{19} is selected from hydrogen, substituted and unsubstituted, branched- and straight-chain alkyl,

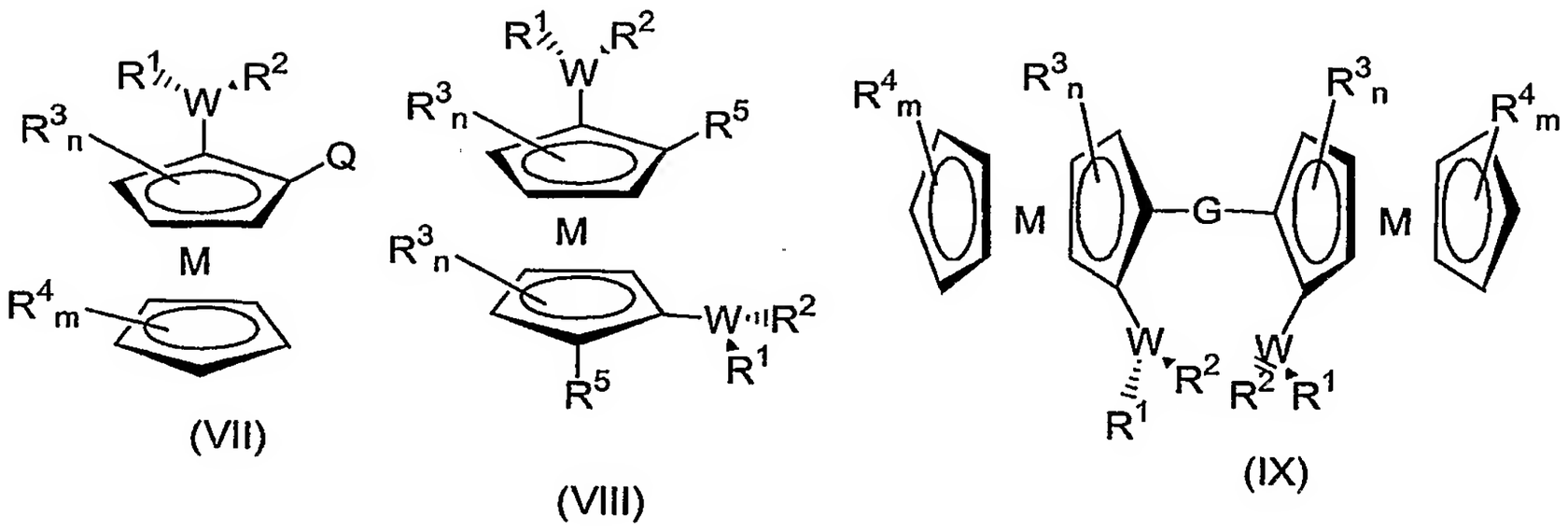
substituted and unsubstituted cycloalkyl, substituted and unsubstituted carbocyclic aryl, and substituted and unsubstituted heteroaryl wherein the or each heteroatom is independently selected from sulphur, nitrogen, and oxygen; or $(R^{19})_2$ is $-(CH_2)_{m'}-$, n' is 0 to 4; and m' is 1 to 8;

2. Enantiomers of the ligands according to claim 1 having the Formulae (IV), (V) and (VI):



wherein each of W, M, R^{1-19}, Q, G, n, m, n' and m' have the same meanings as assigned in claim 1, with chirality changes in the substituent groups where required.

3. Diastereomers of the ligands according to claim 1 having the Formulae (VII), (VIII) and (IX):



(VII) (VIII) (IX)

wherein each of W, M, R^{1-19}, Q, G, n, m, n' and m' have the same meanings as assigned in claim 1, with chirality changes in the substituent groups where required.

4. A metallocene-based phosphine according to any one of claims 1 to 3 having chirality at phosphorus (or arsenic) and at least one other element of chirality (planar chirality and/or chirality at carbon and/or axial chirality).

5. A metallocene-based diphosphine or diarsine ligand according to any one of claims 1 to 4 having three elements of chirality, namely planar chirality, chirality at phosphorus (or arsenic), and chirality at carbon.

6. A metallocene-based diphosphine or diarsine ligand according to any one of claims 1 to 4 having four elements of chirality, namely

planar chirality, chirality at phosphorus (or arsenic), chirality at carbon and axial chirality.

7. A ligand according to any one of claims 1 to 6 wherein the metallocene is ferrocene.

8. A ligand according to any one of claims 1 to 7 wherein W is phosphorus.

10. Use of the ligand of any one of claims 1 to 8 as a catalyst or catalyst precursor in asymmetric transformation reactions to generate high enantiomeric excesses of formed compounds.

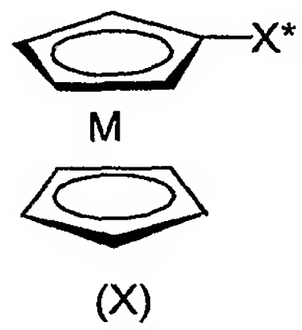
11. A transition metal complex containing a transition metal coordinated to a ligand according to any one of claims 1 to 8.

12. A transition metal catalyst according to claim 11 wherein the transition metal is a Group VIb or a Group VIII metal.

13. A method for preparing a ligand according to any one of claims 1 to 8 comprising providing a metallocene-based substrate having a chiral directing substituent on one or both rings, and subjecting the substituted metallocene to ortho-lithiation followed by converting the

ortho-lithiated substituted metallocene to a phosphine chiral at phosphorus (or to an arsine chiral at arsenic).

14. A method according to claim 13 for preparing the ligand of Formula (I) or (III) comprising providing a compound of the formula (X) (optionally substituted on one or both cyclopentadiene rings with R^3_n (top ring) and/or R^4_m (bottom ring)):

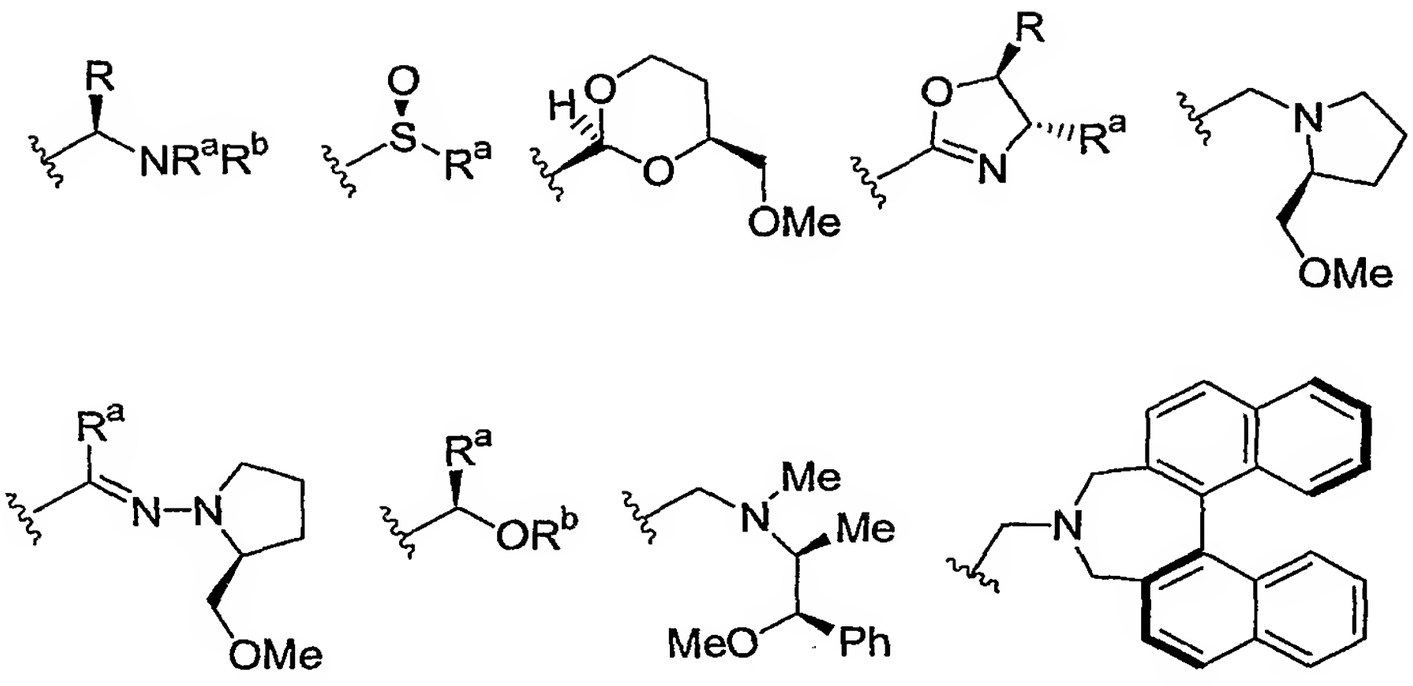


(X)

wherein X* is a chiral directing group;

ortho-lithiating the substrate; reacting the ortholithiated substrate with an R^1 substituted phosphine or arsine, and with an R^2-bearing Grignard reagent or organolithium compound, and converting X* to Q or G as desired.

15. A method according to claim 14 wherein X* is selected from the group consisting of :



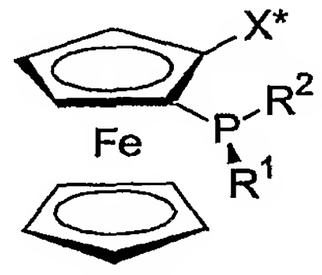
wherein

R^a and R^b are same or different, and are independently selected from hydrogen, substituted and unsubstituted, branched- and straight-chain alkyl, substituted and unsubstituted cycloalkyl, substituted and unsubstituted carbocyclic aryl, and substituted and unsubstituted heteroaryl wherein the or each heteroatom is independently selected from sulphur, nitrogen, and oxygen.

16. A method according to claim 14 or claim 15 wherein the ortho-lithiation step is conducted using n-butyllithium, sec-butyllithium and/or tert- butyllithium.

17. A method according to claim 16 wherein the resulting monolithium compound is reacted *in situ* with a dichlorophosphine of the formula R^1PCl_2 wherein R^1 is as defined in claim 1 to yield an intermediate product.

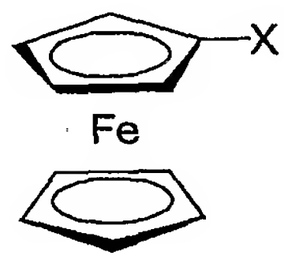
18. A method according to claim 17 comprising reacting the intermediate product with an organometal reagent of the formula R^2Z, wherein R^2 is as defined in claim 1; Z is Li or MgY wherein Y is a halide, to obtain phosphorus chiral compound having formula (XI):



(XI)

19. A method according to claim 18 comprising converting compound XI to compound (I) or (III).

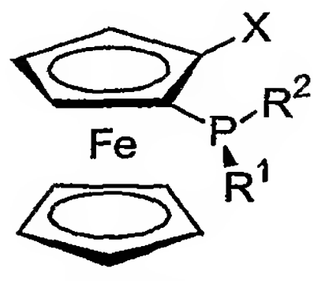
20. A method for preparing the ligand of Formula (I) or (III) comprising providing a compound of the formula XXXVII:



(XXXVII)

wherein X is an achiral directing group and subjecting the compound to enantioselective mono-ortho-lithiation using n-butyllithium or sec-butyllithium or tert- butyllithium in the presence of a homochiral tertiary amine, and reacting the resulting chiral monolithium compound *in situ* with a dichlorophosphine of the formula R^1PCl_2 followed by reacting with an organometallic reagent of the formula R^2Z, wherein R^1 and R^2 are as defined in claim 1; Z is Li or MgY

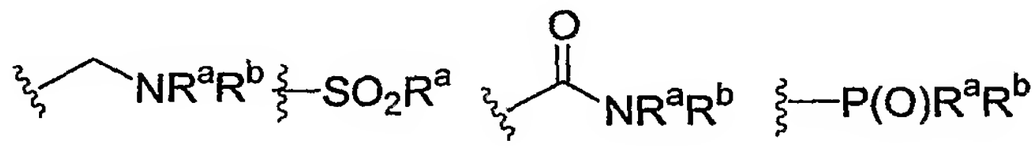
wherein Y is a halide, to obtain a phosphorus chiral compound having formula XXXVIII:



(XXXVIII)

and converting compound XXXVIII to compound (I) or(III).

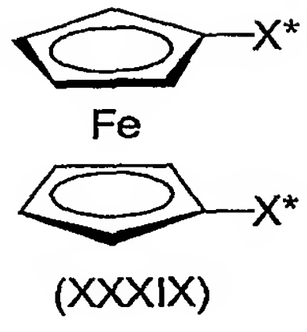
21. A method according to claim 20 wherein X is selected from:



wherein

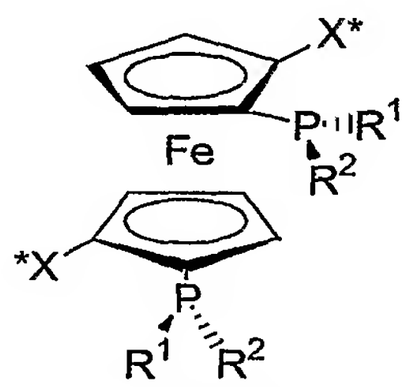
R^a and R^b are same or different, and are independently selected from hydrogen, substituted and unsubstituted, branched- and straight-chain alkyl, substituted and unsubstituted cycloalkyl, substituted and unsubstituted carbocyclic aryl, and substituted and unsubstituted heteroaryl wherein the or each heteroatom is independently selected from sulphur, nitrogen, and oxygen;

22. A method for preparing the ligand of Formula (II) comprising providing a compound of the Formula XXXIX:



(XXXIX)

wherein X* is as previously defined; and subjecting the compound to bis-ortho-lithiation using n-butyllithium, sec-butyllithium or tert-butyllithium, and reacting the resulting bislithium compound *in situ* with a dichlorophosphine of the formula R^1PCl_2 followed by reacting with an organometallic reagent of the formula R^2Z wherein R^1 and R^2 are as defined in claim 1; Z is Li or MgY wherein Y is a halide, to obtain a phosphorus chiral compound having formula XXXX:



(XXXX)

and converting compound XXXX to compound II.